ХІМІЧНІ СЕНСОРИ

CHEMICAL SENSORS

INTERLAYER TRANSFER AND QUENCHING OF EXCITATION ENERGY IN LANGMUIR-BLODGETT FILMS, DEPOSITED ONTO ELECTRODES OF ELECTROCHEMILUMINESCENT SENSOR

Yu. T. Zholudov, N. N. Rozhitskii

Kharkiv National University of Radioelectronics, 61166 Kharkiv, Lenin Av.14; tel. (057)7020369; E-mail: rzh@kture.kharkov.ua

Abstract

EVOLUTION OF MOLECULAR EXCITATION IN ELECTROCHEMILUMINESCENT SENSOR WITH ELECTRODES COVERED BY LANGMUIR-BLODGETT FILMS

Yu. T. Zholudov, N. N. Rozhitskii

Processes of nonradiative excitation energy transfer and excited states quenching in electrochemiluminescent sensor with working electrode, modified by Langmuir-Blodgett film with incorporated electrochemiluminescer molecules, are investigated by means of mathematical modeling. Comparison with experimental results revealed that considered model is applicable for Langmuir-Blodgett films thinner than 10 monolayers. The optimal thickness of the film for electrochemiluminescent sensor operation was estimated as 3-5 monolayers.

Key words: electrogenerated chemiluminescence, Langmuir-Blodgett films, ECL sensor

Анотація

ЕВОЛЮЦІЯ МОЛЕКУЛЯРНОГО ЗБУДЖЕННЯ В ЕЛЕКТРОХЕМІЛЮМІНЕСЦЕНТНОМУ СЕНСОРІ З ЕЛЕКТРОДАМИ, ВКРИТИМИ ПЛІВКАМИ ЛЕНГМЮРА-БЛОДЖЕТ

Ю. Т. Жолудов, М. М. Рожицький

Шляхом математичного моделювання досліджено процеси безвипромінювального переносу енергії збудження та тушіння збуджених станів в електрохемілюмінесцентному сенсорі з робочим електродом, що модифікований плівкою Ленгмюра-Блоджет з інкорпорованими молекулами електрохемілюмінофорів. Порівняння з експериментальними результатами показало, що розглянута модель може застосовуватися для плівок Ленгмюра-Блоджет тонше за 10 моношарів. Знайдена оптимальна товщина плівки для роботи електрохемілюмінесцентного сенсора складає 3-5 моношарів.

Ключові слова: електрогенерована хемілюмінесценція, плівки Ленгмюра-Блоджет, ЕХЛ сенсор

Аннотация

ЭВОЛЮЦИЯ МОЛЕКУЛЯРНОГО ВОЗБУЖДЕНИЯ В ЭЛЕКТРОХЕМИЛЮМИНЕСЦЕНТНОМ СЕНСОРЕ С ЭЛЕКТРОДАМИ, ПОКРЫТЫМИ ПЛЕНКАМИ ЛЕНГМЮРА-БЛОДЖЕТ

Ю. Т. Жолудов, Н. Н. Рожицкий

Путем математического моделирования исследованы процессы безызлучательного переноса энергии возбуждения и тушения возбужденных состояний в электрохемилюминесцентном сенсоре с рабочим электродом, модифицированным пленкой Ленгмюра-Блоджет с инкорпорированными молекулами электрохемилюминофоров. Сравнение с экспериментальными результатами показало, что рассмотренная модель может применяться для пленок Ленгмюра-Блоджет тоньше 10 монослоев. Найденная оптимальная толщина пленки для работы электрохемилюминесцентного сенсора составляет 3-5 монослоев.

Ключевые слова: электрогенерированная хемилюминесценция, пленки Ленгмюра-Блоджет, ЭХЛ сенсор

Introduction

Electrochemiluminescence (ECL) is a kind of non-optically excited luminescence due to sequential electrochemical and recombination processes in electrochemiluminescent device during electrolysis in solutions of organic luminescers [1]. Mentioned phenomenon can be used as powerful analytical tool in biology, medicine, ecology and other areas. With the emergence of nanotechnology the miniature ECL sensors became widely spread [2-4].

Classical ECL systems are mostly based on non-aqueous ECL compositions and use recombination ECL processes, i.e. the excited luminescer molecules are produced from recombination of radical ions electrogenerated at the electrode. The appearance of aqueous ECL, important for different biomedical and ecological applications, was due to discovery of water soluble electrochemiluminescers (first of all luminol – 3-amino-phtalhydrazide and ruthenium tris(2,2′-bipyridine) complex, other ruthenium and osmium complexes are much less spread) as well as due to utilization of ECL reactions with coreactants. The latter solves the problem of simultaneous generation of electrochemiluminescer's radical anions and cations that is difficult due to narrow available potential window of the water (caused by its electrolysis decomposition). ECL reactions with coreactants allow using only one form of radical ion – cation or anion generated on the electrode, the corresponding counter-ion is produced by the coreactant due to its oxidation/reduction by electrode and/or radical ion of the electrochemiluminescer.

In order to overcome limitations implied by aqueous ECL systems there can be used immobilization of electrochemiluminescer at the working electrode of the ECL cell. This can be done by different methods that allow deposition of organic films. The examples of ECL from the films on the electrode containing electrochemiluminescer molecules are known [5-8]. In our previous works [9, 10] we proposed deposition of Langmuir-Blodgett (LB) films with incorporated electrochemiluminescers on the working electrode of ECL sensor to allow use of water-insoluble electrochemiluminescers which considerably extend range of substances that can be used for ECL generation. LB method allows deposition of ordered monomolecular films of amphiphilic molecules and polymers. Since most known inaqueous electrochemiluminescers do not form Langmuir monolayers at the air/water interface they should be included into electrochemicaly inert matrix of amphiphilic molecules or polymer.

Most interesting applications of ECL sensors deal with aqueous analyte solutions (bioliquids, environmental water etc.) that can contain dissolved oxygen and other components — efficient quenchers of the excited states of organic electrochemiluminescers. Quenching effect by those species can strongly reduce efficiency of ECL generation within sensor (and thus analytical signal level and detection limit) especially if the active molecules are immobilized by LB method at the electrode surface, i.e. number of those molecules is small comparing to classical homogeneous ECL systems.

Another process within considered system that can be used to enhance sensor performance is non-radiative excitation energy transfer between electrochemiluminescer molecules located in different LB layers. Since excited molecules within different layers have different separation from the potential quencher the quenching efficiency for those mol-

ecules will be lower for further layers. Thus increase of LB film thickness seems to enhance ECL sensor efficiency, i.e. reduce quenching. From the other hand increase of LB film thickness (number of LB monolayers) leads to decrease of redox current since conductivity of such films is pure.

Considering above stated there should exist some optimal number of LB layers (film thickness) that provides best performance of ECL sensor with working electrode modified by LB film of electrochemiluminescer molecules.

The goal of the present work is to investigate influence of excited electrochemiluminescer molecules evolution due to excitation energy transfer and quenching by the components of the analyte solution on the efficiency of ECL sensor operation.

Excitation energy transfer modeling

The process of nonradiative excitation energy transfer plays important role in different kinds of light emitting devices, incorporating organic active medium [11, 12]. In the considered system of LB matrix doped with electrochemiluminescer molecules there is no immediate contact between donor and acceptor of excitation energy and the most considerable way of energy transfer is Forster transfer. It involves the through-space interaction of the excited donor molecule with a neighboring acceptor molecule. An appropriate description of this process involves the resonant interaction of the transition dipole moments of the donor and acceptor molecules [13]. Forster energy transfer requires spectral overlap of donor fluorescence spectra and acceptor absorption spectra. In the considered case donor and acceptor are the same molecules of incorporated electrochemiluminescer.

In case of electrochemical excitation of active medium the excitation energy is localized on the external monomolecular layer of the film and the energy is distributed through the film due to nonradiative energy transfer [14]. The simplified model of LB film doped by electrochemiluminescer molecules is a lattice, and each molecule of matrix or dopant is situated in the node of this lattice (Fig. 1). On this figure the layers plane corresponds to Y0Z. The energy transfer is assumed to be in x direction perpendicular to electrode plane. The distances between electrochemiluminescer molecules within one layer Δy and Δz are determined by the doping level of organic matrix; Δx value is equal to monolayer thickness and is determined by the type of used matrix.

The structure shown on Fig. 1a has each LB layer identical to the previous one. Such structure is believed to be formed by LB deposition method in case of using amphiphilic matrix molecules, the same composition and deposition parameters of each layer. For polymeric matrixes such behavior is unlikely to be true. There can be found all possible relative positions of donor and acceptor molecules so corresponding recalculation of energy transfer rate is necessary. This can be done by averaging transfer efficiency for film structures corresponding to most favorable and unfavorable case of energy transfer. In the latter structure electrochemiluminescer molecules of the next layer are located just above the center of gap between electrochemiluminescer molecules of the previous layer (Fig. 1b).
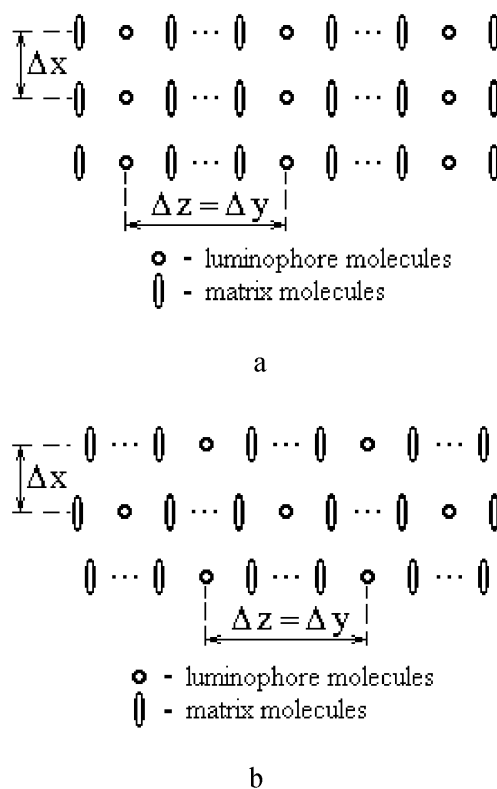

a

b

Fig.1 — Simplified physical model structures of doped LB films

For specified structures the energy distribution can be described using rate equations system — one rate equation for excited states population per monolayer. Each equation accounts processes of energy transfer from and to neighboring layers and spontaneous deactivation of the excited molecules of monolayer. The equation for the first layer should also contain terms for ECL excitation and quenching rates. The account of all neighboring layers for

energy transfer simulation is not required since energy transfer efficiency considerably decreases with distance. In general case such mathematical model (1) with corresponding initial conditions (2) can be written as follows:

$$\begin{cases} \dfrac{dN_1}{dt} = Ex(t) - N_1(t)\left(Q - \dfrac{1}{\tau_S}\right) + \\ \qquad + \sum\limits_{j=2}^{m}\Big(k_L(j-1)\big(N_j(t)-N_1(t)\big)\Big), \\ \dfrac{dN_i}{dt}\bigg|_{i=2\ldots m} = -\dfrac{N_i(t)}{\tau_S} + \\ \qquad + \sum\limits_{\substack{j=1,\\ j\neq i}}^{m}\Big(k_L\big(|j-i|\big)\big(N_j(t)-N_i(t)\big)\Big), \end{cases} \quad (1)$$

$$N_i(0) = 0\big|_{i=1\ldots m}, \qquad (2)$$

where $N_i(t)$ — excited states population in i^{th} layer; m — number of monomolecular layers in the film; $Ex(t)$ — excitation rate of the external monolayer; Q — quenching rate constant of the excited state; $k_L(n)$ — interlayer energy transfer rate constant across n monolayers; τ_S — electrochemiluminescer singlet state lifetime.

Interlayer energy transfer rate constant $k_{L1}(n)$ for system shown on Fig. 1a can be estimated from equation (3). In this equation we assume additivity of nonradiative energy transfer rate for several acceptor molecules, i.e. transfer from one donor molecule to all molecules of acceptor layer. Since Forster constant is strongly dependent on donor-acceptor distance ($\sim R^{-6}$), it is not indispensable accounting all molecules of acceptor layer but only several neighboring ones.

$$k_{L1}(n) \approx k_0 \times$$

$$\times \sum_{s=-N}^{N}\sum_{p=-N}^{N}\left(\sqrt{(n\cdot\Delta x)^2+(s\cdot\Delta y)^2+(p\cdot\Delta z)^2}\right)^{-6}, \quad (3)$$

where n — separation between donor and acceptor monolayers (number of layers); k_0 — Forster energy transfer rate constant for unit distance; $2N+1$ — number of acceptor molecules, accounted in one monolayer in each direction (y and z).

The corresponding rate constant $k_{L2}(n)$ for system shown on Fig. 1b can be estimated from equation (4) as

$$k_{L2}(n) \approx k_0 \sum_{s=-N-1}^{N}\sum_{p=-N-1}^{N}\left(\sqrt{(n\cdot\Delta x)^2+\big((s+1/2)\cdot\Delta y\big)^2+\big((p+1/2)\cdot\Delta z\big)^2}\right)^{-6}, \qquad (4)$$

where $2N$ — number of acceptor molecules, accounted in one monolayer in each direction (y and z).

The energy transfer rate constant $k_L(n)$ (in eq. 1) valid for LB films made of polymeric matrix in first approximation can be found as $(k_{L1}(n)+k_{L2}(n))/2$. Another thing that should be pointed out for polymeric LB film is the computation of k_0 — rate constant of Forster energy transfer for unit distance. Forster transfer rate depends on orientation of donor and acceptor dipole moments through the so called orientation factor κ that can be in the range 0-2. Since in polymeric film spatial orientation of incorporated electrochemiluminescer is not ordered as for the case of LB films formed of amphiphilic monomers the value of orientation factor should be taken as for the case of random orientation of donor-acceptor pairs in a rigid medium, i.e. $\kappa = 0.475$ [15].

Numerical simulation of the considered model can give kinetics of excitation distribution as a response for electrochemical excitation $Ex(t)$ as well as stationary excitation energy distribution through the film doped with electrochemiluminescer. In order to estimate influence of quenching on the device efficiency it is necessary to compute stationary distribution of excited states population for the case of constant excitation rate. The integral of those excited states over film thickness will give efficiency of the device in arbitrary units.

The results of computation are given on Fig.2. The computation was done for organic polymethylmethacrylate matrix doped with 20 molar % of rubrene. The quenching rate constant Q was taken relative to interlayer excitation energy transfer rate constant $k_L(1)$. Parameters of LB films of PMMA, that are necessary for computation, were taken from [16]. The density of rubrene molecules packaging was estimated as 4.55×10^{14} molecules/cm²; film thickness was taken as 5 nm and is based on the results of X-ray photoelectron spectroscopy measurements; referenced results also confirm uniformity and absence of pores in mentioned LB films. The corresponding interlayer excitation energy transfer rate constant $k_L(1)$ is estimated as 2.616×10^{10} s⁻¹.
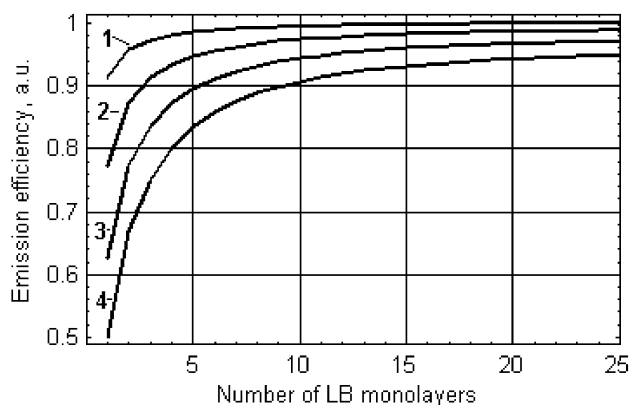
Fig.2 — Emission efficiency of doped LB films of different thickness for different quenching rate of the excited states: 1) $Q / k_L(1) = 0.1$; 2) $Q / k_L(1) = 0.3$; 3) $Q / k_L(1) = 0.6$; 4) $Q / k_L(1) = 1$.

Experimental section

In this study we used LB films of polymeric matrix polymethylmethacrylate (PMMA) with incorporated electrochemiluminescer rubrene deposited onto transparent ITO covered glass electrodes. The electrochemical and ECL measurements were done in bidistilled water with tripropylamine (TPA) as a coreactant and $LiClO_4$ as a supporting electrolyte in usual three electrode electrochemical cell using cyclic voltammetry method (Fig. 3). The 75 mm² ITO coated glass substrates with deposited LB films of rubrene served as working electrodes of the cell. The potential scan vas done in the range $0 \div +1.25$ V vs. Ag/AgCl reference electrode at 100 mV/s. Platinum foil was used as an auxiliary electrode.
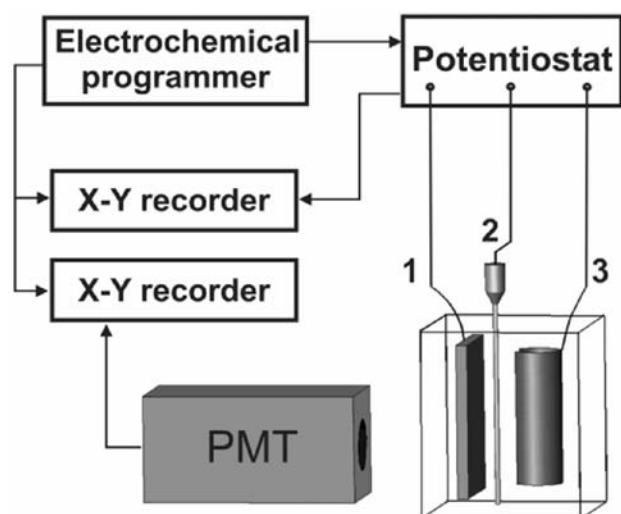

Fig.3 — Scheme of experimental setup. 1 — ITO working electrode; 2 — Ag/AgCl reference electrode; 3 — Pt foil auxiliary electrode.

We have investigated substrates covered with 1, 3, 5, 15 and 50 LB monolayers of PMMA containing 20 molar percents of rubrene. Results for maximal electrochemical current and ECL photocurrent for different samples of ITO electrodes are given on Fig. 4. It is clearly seen that the curve of electrochemical current through the films has several regions with different slope. This can be explained by interplay between different mechanisms of charge transfer through LB films with incorporated electroactive molecules (rubrene) [17]: transfer of charge through molecular orbitals of rubrene due to its oxidation/ reduction, tunneling of charge through the whole film, direct oxidation/reduction of coreactant at the electrode due to its diffusion through pinholes or its penetration into LB film if the latter has insufficient packaging of molecules (strongly depends on the surface pressure of Langmuir monolayer at the air\water interface during deposition of LB film). Analysis of ECL curve of Fig.4 reveals even stronger decay of light intensity with increasing number of LB layers. This is probably due to the fact that not all of the mentioned components of electrochemical current contribute to the creation of ECL emitters (excited rubrene molecules). This hypothesis can be supported by the curve for relative ECL generation efficiency (ratio of ECL photocurrent and electrochemical current) versus film thickness during ECL generation in considered LB films (Fig. 5).
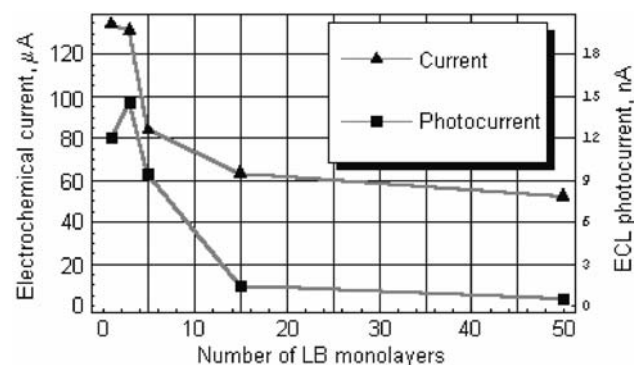

Fig.4 — Maximal electrochemical current and ECL photocurrent for tested ITO samples with LB films containing rubrene in PMMA matrix.

Analysis of obtained results

In order to estimate influence of excitation energy transfer through LB film thickness and excited states quenching on efficiency of ECL generation in the considered system it is necessary to compare results of theoretical computation and experiment.

This can be done by comparing ECL dependence versus LB film thickness and electrochemical current multiplied by theoretically computed ECL emission efficiency curve (Fig. 2). Such comparison allows estimation of excited states quenching rate and applicability area of the developed model. Results of such comparison are given on Fig. 6. On this figure there are given normalized to unity curves for ECL photocurrent ("Experiment" curve) and electrochemical current multiplied by computed ECL emission intensity ("Computation" curve) versus LB film thickness.
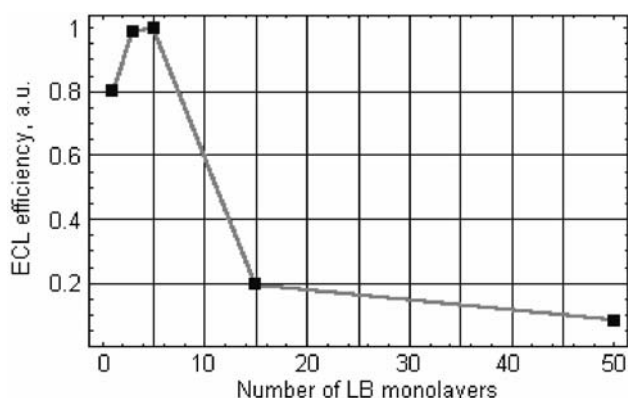

Fig.5 — Relative efficiency of ECL generation for tested ITO samples with LB films containing rubrene in PMMA matrix.
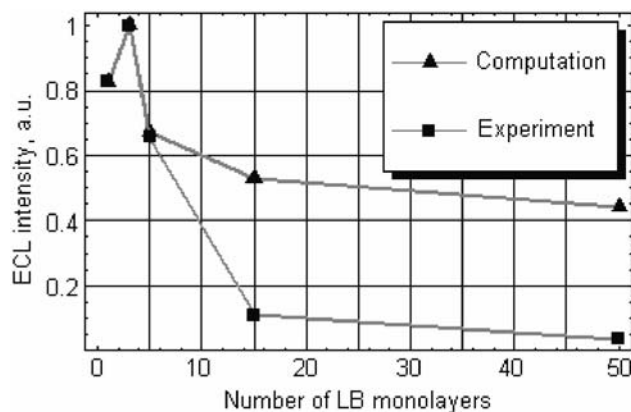

Fig.6 — Relative ECL intensity for tested ITO samples with LB films containing rubrene in PMMA matrix.

Results presented on Fig.6 indicate that developed model of ECL emission efficiency based on excitation energy transfer and excited states quenching by components of solution works fine for small thickness of LB film (about 5÷7 LB monolayers). For ITO electrodes with 1, 3 and 5 LB layers computed results give almost exact matching with observed ECL. For higher film thicknesses some other processes prevail over excitation quenching

and are responsible for ECL intensity decay. Those processes probably cause decrease of ECL emitters' generation efficiency rather than quench already generated excited states. The results on Fig.6 were computed for excitation quenching rate constant $Q = 0.4\,k_L(1) \cong 1.05\times10^{10}$ s^{-1}.

Conclusion

The developed model of excitation energy transfer and excited states quenching by components of solution in LB films doped with electrochemiluminescers showed its applicability for LB films containing up to 5÷7 monolayers. The relative efficiency of ECL generation in such films showed global maximum in the range of 3÷5 monolayers (for conditions used in our experiments) which is the optimal film thickness for ECL sensors creation. Comparison of experimental and computation results showed importance of excitation energy transfer and excited states quenching processes for operation of the considered type of ECL sensors with modified working electrode.

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